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Local study of lithiation and degradation paths in $LiMn_2O_4$ battery cathodes via scanning probe microscopy and confocal raman microscopy

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Lithium manganese-based cathodes ($LiMn_2O_4$, LMO) are widely used in rechargeable batteries due to their low cost, safety, and ecological stability. Enhancement of the LMO properties is impossible to be realized without understanding of nature of the processes occurring inside the cathodes at the nanoscale. In this contribution we studied comprehensively structural and functional transformations of the LMO electrode occurring with its lithiation and degradation via Scanning probe microscopy (SPM) and confocal Raman microscopy.

SPM makes possible studying of the ionic mobility at the nanoscale via local excitation by the biased scanning probe tip, so-called electrochemical strain microscopy (ESM) [1]. We developed novel quantitative ESM approach based on analyzing of frequently dependent electro-mechanical response [2]. ESM measurements showed that Li ions are distributed non-uniformly inside the LMO particles. The average diffusion coefficient in individual particles ~2×10-10 cm^2s^{-1} had a value close to the expected one for fully charged LMO. Enhancement of the concentration in the vicinity of particle boundaries can be attributed to the limited diffusion path of lithium forming an apparent core–shell structure. We registered also about 50% decrease of the diffusion coefficient at thin interface layer of the individuals LMO particles (from a few to tens nanometers).

Structural study of LMO electrodes by spatially resolved Raman spectroscopy showed that cycling leads to: (1) formation of Mn_3O_4 phase with its further dissolution in the electrolyte; (2) qualitative change of the lithiation process in cycled LMO cathodes with formation of the significant inhomogeneous lithiation state. Spatial distribution of Mn_3O_4 phase was spatially correlated with the cracks on the particles surface revealed by optics, which means that appearance of Mn_3O_4 phase can be responsible for the mechanical stresses in the material. The segregation of Mn_3O_4 phase was found as well in vicinity of the particle boundaries and thereby determine diminished electrochemical activity. On contrary, Mn_3O_4 phase was not revealed in aged cathodes, which prove that the dissolution of this phase occurs mostly at the beginning of cycling while further mechanism of capacitance fade is due to inhomogeneity of the delithiation process [3].

Thereby the final model of the material could be following: structural transformation with formation of the weak electrochemically active phase near the particle interface lead to the impeding of lithiation process and formation of inhomogeneous distribution of the ‘state of charge’. This inhomogeneity increases self-consistently during lithiation process regardless dissolution of the additional phases possibly due to impact of chemically induced stresses. The inhomogeneous lithiation is than believed to be responsible for the capacity fade in the battery.

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